

Supporting Information

Fabrication, Testing and Simulation of All Solid State Three Dimensional Li-ion Batteries

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Pillar fabrication

A thin layer of hexamethyldisilazane (HMDS) was coated on Si wafer in a HMDS prime oven at 150 °C for 5 min, followed by spin-coating of photoresist at a speed of 4000 min⁻¹ (4000 revolutions per minute) for 1 min, then soft-baked at 115 °C for 1 min. The resulting wafer was placed into a commercial contact mask aligner together with our custom-designed mask and then illuminated with a broadband source with an energy dose of 125 mJ cm⁻² in vacuum contact mode. The wafer was then treated with a developer for 1 min and thoroughly rinsed with deionized H₂O.

Reactive ion etching (RIE): The patterned wafer was placed in a vacuum oven at 90 °C for 30 min to remove the remaining solvent and resist. After 1 min of O₂ plasma treatment with reactive ion etching to ensure the removal of the residual resist, the wafer was placed under O₂ (7.5 cm³/min) and SF₆ (52 cm³/min) plasma for etching Si. The height of the Si pillars was controlled by varying the etching time while maintaining the other conditions the same. After the sample was removed from the RIE chamber, the remaining resist was removed by ultrasonication

the wafer in an acetone bath for 15 min, followed by placing in a bath of post-etch residue remover for 20 min at 90 °C.

LiCoO₂ Raman spectroscopy characterization

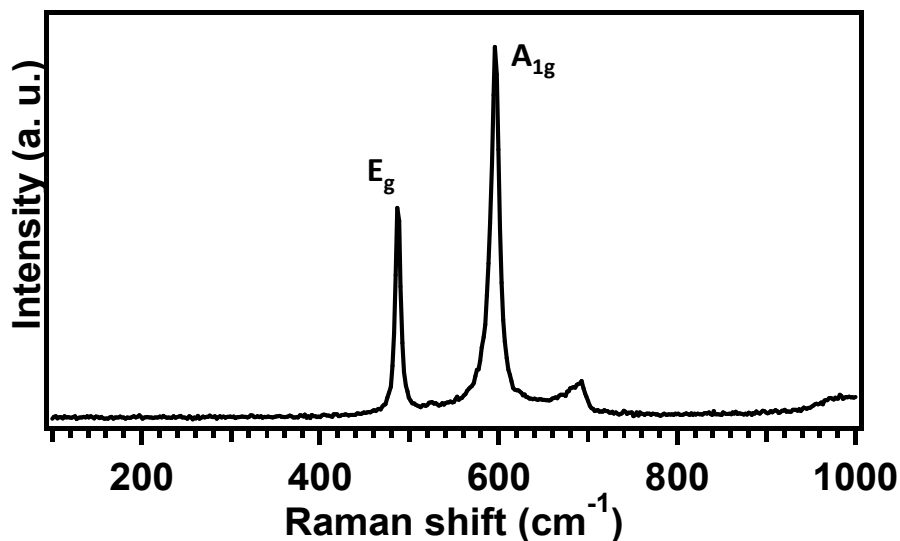


Figure S1. Raman spectra collected using 532 nm excitation with ≈ 0.1 mW laser power measured at the sample. Spectrum is consistent with HT LiCoO₂ phase¹

3D Solid state Li-ion battery on cylindrical microcolumns

Example of 3D solid state Li-ion battery fabricated on scaffolding of Si cylindrical microcolumns using the same process as described in the text. The measured capacity for the 3D battery is $\approx 1/6$ that of a planar SSLIB.

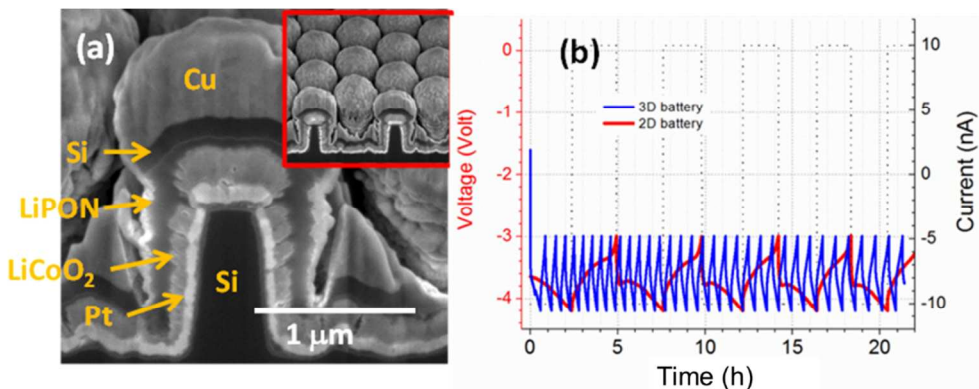


Figure S2. (a) Focused ion beam generated cross section of a 3D SSLIB fabricated on cylindrical Si/SiO₂ microcolumns. (b) Galvanostatic charge discharge curves for the 3D SSLIB and a planar (2D) SSLIB fabricated at the same time. The current density is 5.1 $\mu\text{A}/\text{cm}^2$ for both batteries.

Accuracy of charge capacity measurements

The electrochemical charge/discharge cycling was performed with high precision instrumentation with 1 fA current sourcing resolution, 1 mV voltage (potential) resolution and 1 s time resolution, which translated into an accuracy of $\pm 0.02 \text{ mAh}/\text{cm}^2$ for charge capacity determination. Nevertheless, because too few planar and 3DSSLIBs were measured in this study to calculate standard deviations, the reported capacities are preceded with the “ $\approx$ ” symbol to indicate that these are approximate values, and that we are mainly concerned with demonstrating and understanding the difference in the capacity measured at different charge rates between the planar and 3D structured solid state batteries.

Electrochemical impedance spectroscopy (EIS).

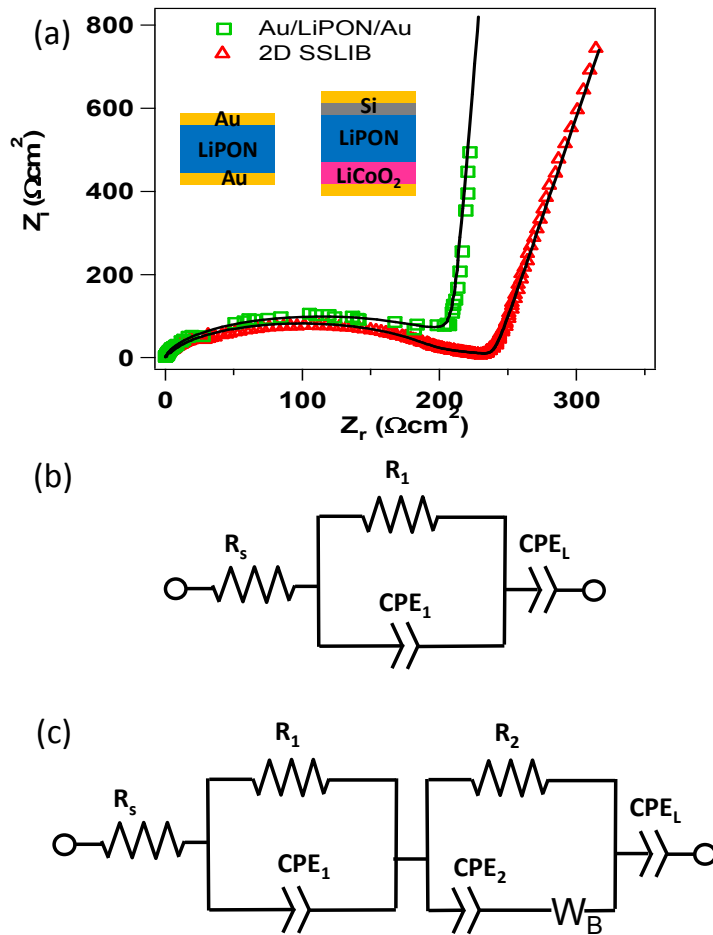


Figure S3. (a) EIS collected for a planar thin film (2D) SSLIB and an Au/LiPON/Au sample that was prepared simultaneously with the battery. Equivalent circuits used for fitting EIS data for (b) Au/LiPON/Au and (c) Pt/LiCoO₂/LiPON/Si/Cu.

Table S1. Parameters extracted from fitting EIS for planar SSLIB

Au/LiPON/Au	value
Thickness (cm)	5.8×10^{-5}
Area (cm ²)	6.6×10^{-4}
R _s (Ω)	~0
R ₁ (Ω)	3.6×10^5
Y _o CPE ₁ (F cm ⁻²)	1.7×10^{-10}
a CPE ₁	0.99
Y _o CPE _L (F cm ⁻²)	3.1×10^{-9}
a CPE _L	0.95
SSLIB	value
Area (cm ²)	2.23×10^{-2}
Thickness LCO (cm)	2×10^{-5}
Thickness LiPON (cm)	5.8×10^{-5}
Thickness (Si) (cm)	0.5×10^{-5}
R _s (Ω)	~0
R ₁ (Ω)	8.0×10^3
Y _o CPE ₁ (F cm ⁻²)	1.9×10^{-9}
a CPE ₁	0.89
R ₂ (Ω)	2.1×10^3
Y _o CPE ₂ (F cm ⁻²)	2×10^{-6}
a CPE ₂	0.61
Y _o W _b (F cm ⁻²)	2×10^{-6}
B W _b	3.3
Y _o CPE _L (F cm ⁻²)	4.7×10^{-5}
a CPE _L	0.93

Finite Element Simulations

The time-dependent transport of Li ions in a 2D axial symmetric geometry based on the 3D SSLIB battery geometry and material properties, as well as in a 1D geometry based on the planar SSLIB, was simulated using commercial finite element simulation program running on a desktop PC. The 2D axial symmetric geometry is shown in the main text, for the simulation of

the 3D SSLIB, which encompasses the LiPON electrolyte, the LiCoO₂ cathode and the Si anode. The planar SSLIB was simulated as a 1D geometry, as shown in Figure S3 (a).

The diffusion and migration of Li ions within the LiPON electrolyte was described by the Nernst-Planck equation with electroneutrality, and is given by:

$$\frac{\partial c_i}{\partial t} + \nabla(-D_i \nabla c_i - z_i \frac{D_i}{RT} F c_i \nabla \varphi) = 0,$$

$$\sum z_i c_i = 0,$$

where c_i is the concentration of species i (either c_{Li+} for Li ions or c_n for the counter ion species used to maintain electroneutrality), D_i is the diffusion coefficient in LiPON for species i , z_i is the charge on species i , φ is the solution potential, R is the gas constant, T is the temperature and F is Faraday's constant.

The mass transport of Li ions within the LiCoO₂ cathode and the Si anode was described by diffusional transport only, and is given by:

$$\frac{\partial c_{Li}}{\partial t} + \nabla(-D_{Li} \nabla c_{Li}) = 0,$$

where c_{Li} is the concentration of Li ions in the cathode or the concentration of Li ions in the anode, D_{Li} is the diffusion coefficient of Li ions in the LiCoO₂ cathode or the Si anode. The diffusion of lithium in the cathode is anisotropic, with the diffusion laterally along the cathode less than the diffusion normal to the cathode. Figure S5 shows the normal and lateral diffusion directions in the 2D cathode.

Li-ion transfer across the anode/electrolyte boundary (boundary 1 in Fig. S4 (a) and (b)) and cathode/electrolyte boundary (boundary 3 in Fig. S4 (a) and boundary 3 in Fig. S4 (b)) was

described using Butler-Volmer kinetics. The flux of Li ions across the anode/electrolyte boundary was described by:

$$j_{anode} = j_{anode}^0 \left(e^{-\alpha_{anode} \frac{F}{RT} \eta_{anode}} - e^{(1-\alpha_{anode}) \frac{F}{RT} \eta_{anode}} \right),$$

where j_{anode}^0 is the exchange flux density, α_{anode} is the charge transfer coefficient, and η_{anode} is the activation overpotential. j_{anode}^0 was defined as:

$$j_{anode}^0 = Fk_{anode} \left(\frac{(c_{Li_anode_max} - c_{Li_anode})c_{Li+}}{c_{Li_anode_max}c_{Li+}^0} \right)^{\alpha_{anode}} \left(\frac{c_{Li_anode}}{c_{Li_anode_max}} \right)^{1-\alpha_{anode}}$$

where k_{anode} is the Li-ion transfer rate constant the anode, c_{Li+}^0 is the initial concentration of Li ions in the electrolyte, $c_{Li_anode_max}$ is the maximum Li-ion concentration in the anode, and

c_{Li_anode} is the Li-ion concentration in the anode. The activation overpotential is defined as

$\eta_{anode} = \phi_{anode} - \phi - E_{anode}$, where the anode potential is ϕ_{anode} . The solution potential, ϕ , at the

anode is set to 0 V. The equilibrium potential for the anode, E_{anode} , as a function of lithiation

ratio ($x = c_{Li_anode} / c_{Li_anode_max}$), including a 70 mV hysteresis in the equilibrium potential

(which reduces the equilibrium potential by 70 mV on a charge cycle and increases the

equilibrium potential by 70 mV on a discharge cycle), can be parametrically fitted with

numerical function $F_{anode}(x)$,²:

$$F_{anode}(x) = -4.76 \cdot (x^6) + 9.34 \cdot (x^5) - 1.8 \cdot (x^4) - 7.13 \cdot (x^3) + 5.8 \cdot (x^2) - 1.94 \cdot (x) + 0.62 \pm 0.07$$

The flux of Li ions across the cathode/electrolyte boundary was similarly described using Butler-Volmer kinetics, as:

$$j_{cathode} = j_{cathode}^0 \left(e^{-\alpha_{cathode} \frac{F}{RT} \eta_{cathode}} - e^{(1-\alpha_{cathode}) \frac{F}{RT} \eta_{cathode}} \right)$$

where $j_{cathode}^0$ is the exchange flux density, $\alpha_{cathode}$ was the charge transfer coefficient, and $\eta_{cathode}$ is the activation overpotential. $j_{cathode}^0$ was defined as:

$$j_{cathode}^0 = Fk_{cathode} \left(\frac{(c_{Li_max} - c_{Li})c_{Li+}}{(c_{Li_max} - c_{Li_min})c_{Li+}^0} \right)^{\alpha_{cathode}} \left(\frac{(c_{Li} - c_{Li_min})}{(c_{Li_max} - c_{Li_min})} \right)^{1-\alpha_{cathode}}$$

and

$$\eta_{cathode} = \phi_{cathode} - \phi - E_{cathode}$$

where c_{Li_max} is the maximum concentration of Li ions in the cathode, c_{Li_min} is the minimum concentration of Li ions in the cathode and $k_{cathode}$ is the Li-ion transfer rate constant at the cathode. Both cathode and anode were assumed to be pure electronic conductors and so have the same electrode potential, $\phi_{cathode}$ or ϕ_{anode} , everywhere. Also, the equilibrium potential of the LiCoO₂, $E_{cathode}$, depends on the composition of the electrode. The equilibrium potential can be expressed numerically as a function $F_{cathode}(x)$ of local Li-ion concentration ratio:

$$F_{cathode}(x) = \frac{-219.027 + 322.003 \cdot x^2 - 198.242x^4 + 354.911x^6 - 467.807x^8 + 207168x^{10}}{-44.337 + 35.463x^2 - 3.4302x^4 + 113.081x^6 - 182.567x^8 + 80.3097x^{10}}$$

where x is the cathode lithiation ratio (which varies between 0.5 and 1). This expression is based on experimental data.³

We apply two additional constraints in the simulation that constrain the total current passed across the anode/electrolyte interface or the cathode/electrolyte interface be constant and equal to the desired charge or discharge rate, i . This can be expressed as:

$$\frac{i}{F} = \int_{\text{Anode/Electrolyte}} j_{\text{anode}} = \int_{\text{Cathode/Electrolyte}} j_{\text{cathode}}$$

The flux of Li ions across the anode/electrolyte boundary, as described above, was applied to the boundary as shown in Fig. S4 (a) and (b). The flux of Li ions at the cathode/electrolyte interface was applied to the boundary labelled in Fig. S4 (a) and (b). All other boundaries are described as no flux boundaries, and are labelled as such in Fig. S4 (b). The initial conditions, at a fully discharged state, for the time dependent simulations are: 20 mol/L Li ions in the electrolyte; 50 mol/L Li ions in the cathode; and 3 mol/L Li ions in the anode. The values of the other physical constants defined above are given in Table S2 below.

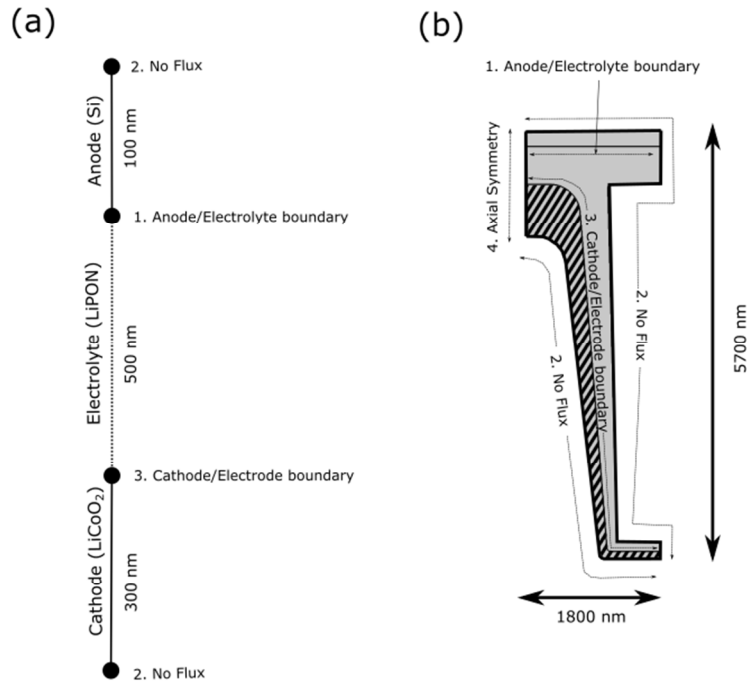


Figure S4. (a) Geometry for the 1D simulation of the planar SSLIB. (b) Boundaries for the 2D simulation of the 3D SSLIB.

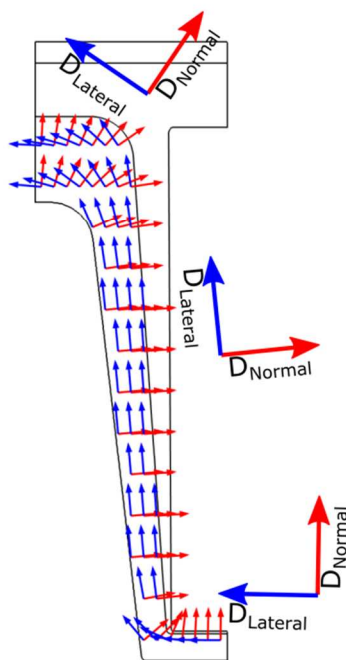


Figure S5. Normal (red) and lateral (blue) directions of the anisotropic diffusion of lithium in the cathode.

Table S2 Parameters used in the finite element analysis

Physical Constant	Description	Value
D_{Li+}	Diffusion coefficient of Li ions in LiPON electrolyte	$1.66 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$
D_n	Diffusion coefficient of counter-ions in LiPON electrolyte	$1.66 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$

$D_{\text{Li_normal}}$	Normal diffusion coefficient of Li ions in LiCoO ₂ cathode	3D Sim: $2.5 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ 1D Sim: $4 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$
$D_{\text{Li_lateral}}$	Lateral diffusion coefficient of Li ions in LiCoO ₂ cathode	$1 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$
$D_{\text{Li_anode}}$	Diffusion coefficient of Li ions in the Si anode	$1 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$
z_{Li^+}	Charge on Li ions in LiPON electrolyte	+1
z_{n}	Charge on counter ion in LiPON electrolyte	-1
α_{anode}	Charge transfer coefficient at anode	0.5
α_{cathode}	Charge transfer coefficient at cathode	0.5
$c_{\text{Li_max}}$	Maximum concentration of Li ions in the LiCoO ₂ cathode	50 mol/L
$c_{\text{Li_min}}$	Minimum concentration of Li ions in the LiCoO ₂ cathode.	$0.5 \cdot c_{\text{Li_max}}$
$c_{\text{Li_anode_max}}$	Maximum concentration of Li ions in the Si anode	311 mol/L
k_{anode}	Li-ion transfer rate constant for the anode/electrolyte boundary	$1 \times 10^{-2} \text{ mol m}^{-2} \text{ s}^{-1}$

k_{cathode}	Li-ion transfer rate constant for the cathode/electrolyte boundary	$1 \times 10^{-4} \text{ mol m}^{-2} \text{ s}^{-1}$
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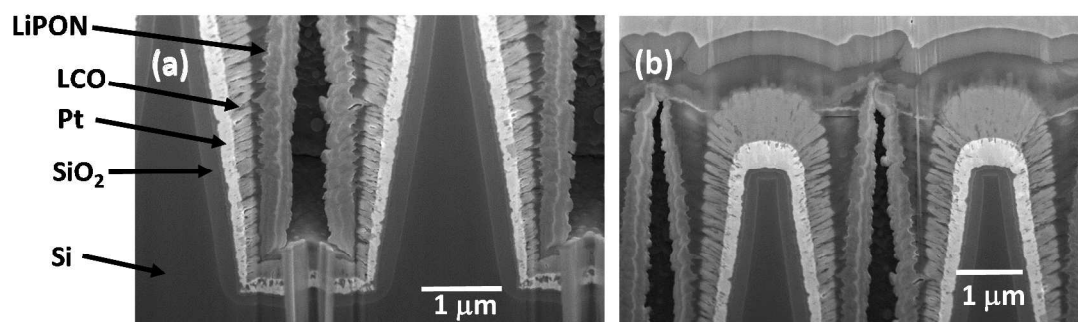


Figure S6. Higher magnification images of the FIB cross section of the bottom (a) and top (b) of the 3DSSLIBs shown in Fig. 1g.

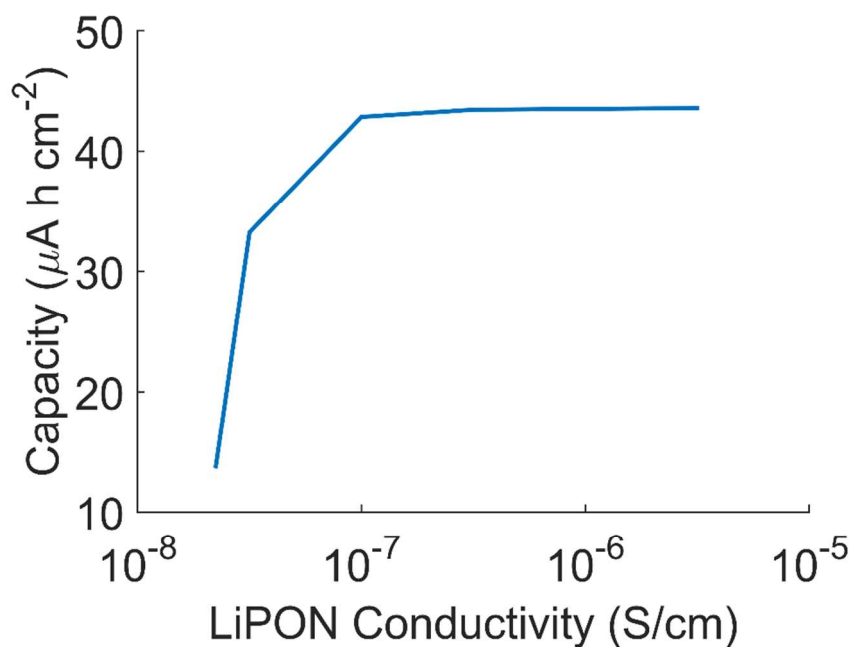


Figure S7. Simulated capacity at a 1C-rate for a range of LiPON conductivities, highlighting significant loss of capacity at electrolyte conductivities of less than $1 \times 10^{-5} \text{ S/cm}$.

References

1. Baddour-Hadjean, R.; Pereira-Ramos, J. P., Raman Microspectrometry Applied to the Study of Electrode Materials for Lithium Batteries. *Chem. Rev.* **2010**, *110* (3), 1278-1319.
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